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Photon-Gated Spectral Hole-Burning Via Donor-Acceptor Electron Transfer

by

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PHOTON-GATED SPECTRAL HOLE BURNING
VIA DONOR-ACCEPTOR ELECTRON TRANSFER

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ABSTRACT: We have observed photon-gated spectral hole-burning (i.e., enhanced hole production in the presence of an additional gating light source) for a derivative of zinc-tetrabenzoporphyrin in poly(methyl methacrylate) thin films in the presence of chloroform acceptor molecules. Gated holes form when single frequency laser radiation excites the 0-0 singlet absorption at 630 nm simultaneous with triplet-triplet excitation by the gating light, with the largest gating enhancement occurring near 480 nm. The gating action spectrum suggests that the mechanism is electron transfer from an excited triplet of the porphyrin donor to the chloroform acceptor. This is the first clear example of persistent spectral hole-burning via donor-acceptor electron transfer; further, the photon-gating characteristics can be modified by altering the acceptor concentration.

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Recent research on mechanisms for persistent spectral hole-burning (PHB) in inhomogeneously broadened transitions at low temperatures has concentrated on photon-gated processes, where spectral hole formation occurs only in the presence of an additional gating light source [1] [2] . Such two-color mechanisms provide new examples of low temperature photochemistry in solids and extend the applicability of spectral hole-burning as a tool for high resolution laser spectroscopy. In addition, since single-photon mechanisms for hole-burning have serious limitations for frequency domain optical storage applications [3] [4] [5] due to destructive readout [6] , photon-gating is considered a crucial requirement for practical data storage and retrieval [7].

The first examples of photon-gated PHB involved two-step photoionization of Sm^{2+} ions in BaClF [1] or carbazole molecules in boric acid glass [2]. Here the first photon produced frequency-selective excitation within the inhomogeneously broadened absorption line; the absorption of a second photon by a long-lived intermediate state resulted in photoionization and thus a decrease in absorption (a spectral hole) at the wavelength of the first photon. Photon gating via two-step photoionization has also been observed for a transition-metal-doped spinel [8]. More recently, a photoadduct of anthracene and tetracene has been observed to undergo photon-gated PHB via a two-step photodissociation reaction [9]. Except for the last example, all these previous cases involve the ejection of an electron from the excited chromophore and the subsequent trapping of the electron at some defect in the host matrix that cannot be easily controlled.

In this paper we report the first observation of PHB via donor-acceptor electron transfer from an excited donor chromophore to a specific acceptor molecule, whose concentration can be modified. In addition, the mechanism shows the novel property of photon-gating. The

specific material consists of a tetrabenzoporphyrin derivative,

meso-tetra(p-tolyl)-Zn-tetrabenzoporphyrin (TZT) in a poly(methylmethacrylate) (PMMA)

host matrix, in the presence of chloroform ($CHCl_3$) acceptor molecules. In one previous

report, two-color "hole-burning" (without scanning of spectral holes) was reported for TZT

in uncharacterized PMMA with no added acceptors [10]. We find that TZT in purified

monodisperse PMMA does not show photon-gating; rather, only shallow one-color

photophysical holes occur. However, in the presence of high concentrations of chloroform

acceptor molecules, deep two-color holes form under a variety of conditions in which one-color

holes are unobservable. In contrast to photoionization in organic molecules [2] where

ultraviolet excitation is normally required for electron ejection, the presence of the acceptor

dramatically lowers the total energy required for electron transfer, allowing convenient

wavelengths in the red to be used for site selection. Photon-gated PHB also occurs for TZT

and its magnesium analog in PMMA with other halomethane acceptors with different electron

affinities, and a systematic study of the influence of several acceptors on both donors will be

the subject of a separate publication [11]. While the identification of suitable materials for

frequency domain optical storage represents a complex optimization problem [7], the ability

to independently vary the donor and acceptor properties greatly expands the parameter space

of possible materials.

The TZT donor molecule was synthesized and purified by extraction and liquid

chromatography [11]. The PMMA host was high purity monodisperse material from Polymer

Laboratories with $M_p \simeq 107,000$ and $M_w/M_n < 1.10$. Particular care was taken to select a

host material free of contaminants such as initiators, stabilizers, and the like. The $CHCl_3$ was

Omnisolv glass distilled spectrophotometric-grade material from EM Laboratories. To prove

that trace concentrations of 2-pentene stabilizer in this solvent were not responsible for the

observed results, gated PHB was also performed on samples made with Aldrich HPLC grade

chloroform stabilized with 0.75% ethanol; no difference was observed. Samples were prepared by dissolution of the TZT and PMMA separately in chloroform, mixing, and partial evaporation of the solvent at 55 C between glass or fused silica plates to a thickness of 75 μm with optical density 0.3-0.8. In identical samples prepared without chloroform, no photon-gated PHB was observed. All measurements were performed at 1.4 K with the samples immersed in superfluid helium.

Figure 1 illustrates the energy levels and the most probable mechanism for the observed photon-gated PHB. The first wavelength, λ_1, (generated by a single-frequency cw dye laser of 3 MHz linewidth) excites the 0-0 component of the $S_1 \leftarrow S_0$ transition of those TZT molecules that are within one homogeneous linewidth of the laser frequency. In the PMMA host matrix, the singlet absorption origin is roughly 300 cm^{-1} wide centered at 627 nm. Since TZT is a fairly rigid chromophore the transition is predominantly zero-phonon in character, and in fact hole spectra taken with a monochromator over a 75 cm^{-1} range show no observable phonon side holes.

To estimate the photophysical rates for TZT we use the published data for unsubstituted Zn-tetrabenzoporphyrin [12] [13] . Thus the fluorescence lifetime from S_1 would be expected to be near 4 ns with a fluorescence yield of 0.2. From S_1 the excited molecules also undergo intersystem crossing to the lowest triplet state, T_1, with high yield ($\simeq$ 0.8). This high yield coupled with a fairly long triplet lifetime of 40 ms allows a large population of triplets to be formed. If the second wavelength, λ_2, is not present, the excited molecules eventually return to the singlet ground state without reaction. We have directly measured [11] the triplet lifetime for TZT/PMMA/CHCl$_3$ system at low temperatures and find 39 ms, which suggests that the photophysical rates for our case are not very different from those for the unsubstituted molecule.

However, if the gating light at λ_2 is present while the molecules are in T_1, triplet-triplet (T-T) transitions can occur for appropriately chosen values of λ_2. Single line radiation from an Ar^+ or a Kr^+ cw laser provides λ_2 values of 351, 413, 488, 514, 647, 676, 752, and 799 nm in a 4 mm diameter spot coincident with the 4 mm diameter λ_1 spot. From an excited triplet state of the donor T_n, the electron is transferred to the acceptor molecule, chloroform. Hole detection is subsequently performed by scanning λ_1 and detecting the sample transmission with a precision ratiometer and an averaging oscilloscope [14]. In all cases, the laser intensity during hole detection was $\simeq 10$ nW.

Figure 2 shows an example of photon-gated PHB for the case of $\lambda_2 = 488$ nm and a sample with a large excess of chloroform. In all cases, the λ_1 power during burning was 2 μW. Trace (a) shows the optical density of the sample after 6 s irradiation with only λ_1 present (at 0 GHz); no observable hole is formed. Trace (b) (of a fresh spectral region nearby) shows that a shallow one-color hole eventually forms after 300 s of irradiation at the same power level. Again using a fresh region of the spectrum, trace (c) shows that a deep hole is formed in 6 s if λ_2 at a power level of 17 mW excites the sample at the same time as λ_1. The presence of λ_2 clearly enhances the formation of the spectral hole.

To be more quantitative about the gating enhancement factor, one would like to define the gating ratio, G, as the two-color hole depth divided by the one-color hole depth for equal λ_1 burning times. However, in a case like Fig. 2 (a), the one-color hole is too shallow to be detected. If longer λ_1 irradiation times are used, one-color holes eventually form, but since hole growth is in general nonlinear in time, it is misleading to linearly extrapolate the one-color hole depth back to 6 s burning times. All that can be correctly concluded from Figure 2 is that the gating ratio is clearly greater than 30, limited by the signal-to-noise ratio.

For the case of λ_2 = 514 nm, the gating ratio is optimal for gating light powers near 20 mW. At lower powers, G decreases presumably due to insufficient excitation in the triplet manifold, whereas at higher powers shallower and broader gated holes are formed due to residual absorption of the gating light in the singlet manifold and subsequent sample heating. In addition, as more and more gated holes are burned in the inhomogeneously broadened line with high gating powers (> 20 mW), the gating ratio decreases by up to 20-40% due to a fatigue effect.

To confirm the role of the triplet states in the hole formation mechanism, the action spectrum of the gating light was measured as shown in Figure 3. The open circles in the figure show the gating ratio measured at various gating wavelengths λ_2 under the condition of constant photon flux for each measurement. The solid line shows the triplet-triplet absorption spectrum for Zn-tetrabenzoporphyrin from Reference [15]. Since the gating action spectrum follows the T-T absorption fairly closely, we conclude that λ_2 is most likely absorbed by T_1 to produce the photon gating and that the quantum yield per gating photon does not vary too strongly with gating photon energy.

The role of the chloroform acceptor molecules was established by the observation that the gating ratio dropped to 1 for samples prepared with no chloroform. The gating ratio was largest for samples with the highest concentration of the acceptor. In the best samples, only a small amount of the chloroform solvent was driven away during the sample preparation process, leaving a fairly "wet" sample. Removal of some amount of the solvent is desirable, however, in order to prevent a cloudy translucence in the sample upon cooling.

To quantify the concentration of chloroform in the prepared samples, infrared spectra of samples prepared between NaCl plates were acquired over the range 600 - 700 cm^{-1}. The extinction coefficients of two lines of the C-Cl stretch at 672 cm^{-1} and at 630 cm^{-1} were

determined to be 33 l/mole-cm and 1.0 l/mole-cm, respectively. The best gating ratios occurred for samples with chloroform concentrations near 10 M, especially when the ratio of $CHCl_3$ to TZT was large, i.e., near 10^5. This suggests that the photoreaction is favored when the largest number of excess chloroform molecules are located near the donor molecule. This is to be expected since the optimal TZT-$CHCl_3$ distance and orientation occurs only for a small fraction of the total number of acceptor molecules in the sample. These results clearly demonstrate that the gating ratio can be controlled by varying the concentration of the acceptor.

Previous photochemical studies of related Zn-porphyrins in matrices containing carbon tetrachloride [16] [17] [18] establish that the photoejected electron can be accepted by the CCl_4, which then undergoes dissociative electron detachment of the form

$$e^- + CCl_4 \rightarrow \dot{C}Cl_3 + Cl^-. \tag{1}$$
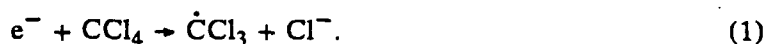
We believe that a similar reaction is responsible for the photon gating observed for the TZT/PMMA/$CHCl_3$ system:

$$TZT \xrightarrow{h\nu_1, h\nu_2} TZT^+ + e^- \tag{2}$$

$$CHCl_3 + e^- \rightarrow \dot{C}HCl_2 + Cl^-. \tag{3}$$
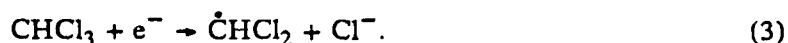
Strong evidence for this comes from measured transmission spectra over a 300-850 nm range of the photoproduct absorption [11], which show similarities to the cation spectrum of Mg-tetrabenzoporphyrin [19]. Preliminary attempts to reverse the electron transfer by irradiating the cation directly have proved unsuccessful. It may be that the reaction of the

chloroform with the ejected electron prevents the reverse electron transfer process, thus forming apparently irreversible persistent holes.

In conclusion, we have observed the formation of gated spectral holes via donor-acceptor electron transfer for the first time using the $TZT/PMMA/CHCl_3$ material and simultaneous singlet-singlet and triplet-triplet excitation. The gating ratio depends strongly on the wavelength of the second photon in a fashion that mimics the T-T absorption of the donor. The gating ratio can also be controlled by varying the concentration of the chloroform acceptor. It is expected that the results reported here will stimulate a search for new examples of photon-gated and single-photon PHB in which donor-acceptor electron transfer is responsible for hole formation. In particular, carefully selected rigidly linked donor-acceptor molecules [20] in which the donor-acceptor distance can be carefully controlled are possible candidates.

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FIGURE CAPTIONS

Figure 1. Level diagram for photon-gated PHB via donor-acceptor electron transfer. The structure of the donor chromophore TZT is shown in the inset.

Figure 2. Example of photon gated PHB for the TZT/PMMA/CHCl$_3$ material. (a) Attempt to burn one-color hole with 6 s burn time with λ_1 = 630.173 nm, (b) One-color hole produced after 300 s burn time with λ_1 = 630.724 nm, (c) Photon-gated two-color hole produced after 6 s irradiation with λ_1 = 630.764 nm and λ_2 = 488 nm. The scale is appropriate for trace (c), and traces (a) and (b) have been offset vertically for clarity.

Figure 3. Action spectrum of photon gating for λ_2 (open circles). The solid line represents the T-T absorption from Reference [15]. The chloroform concentration was lower than in Fig. 2.
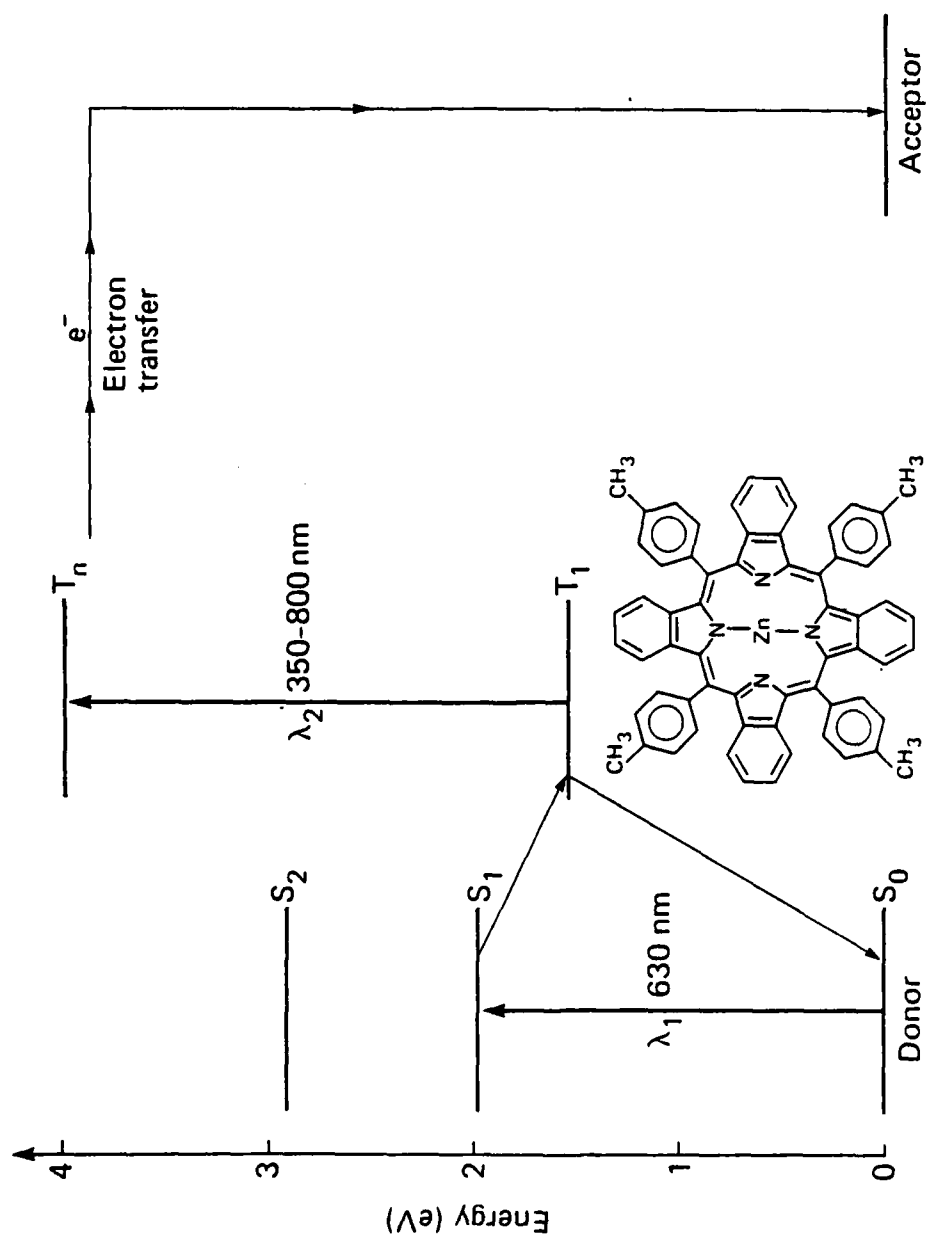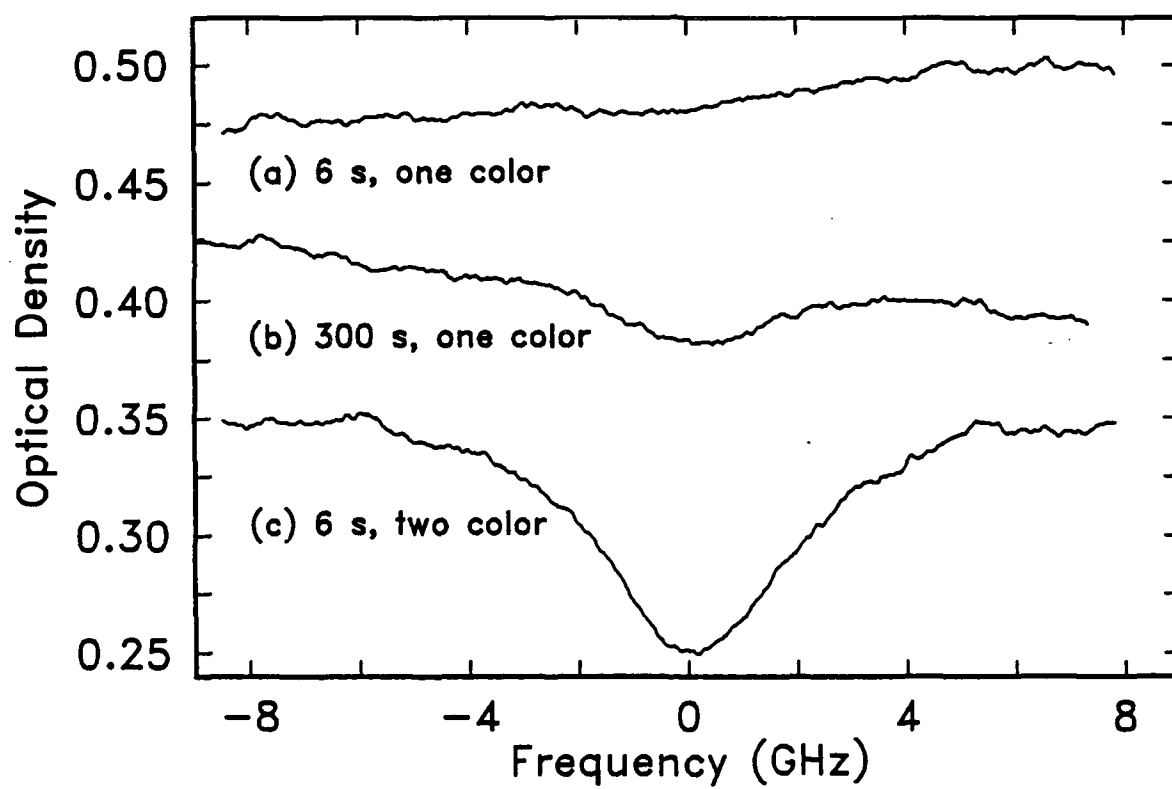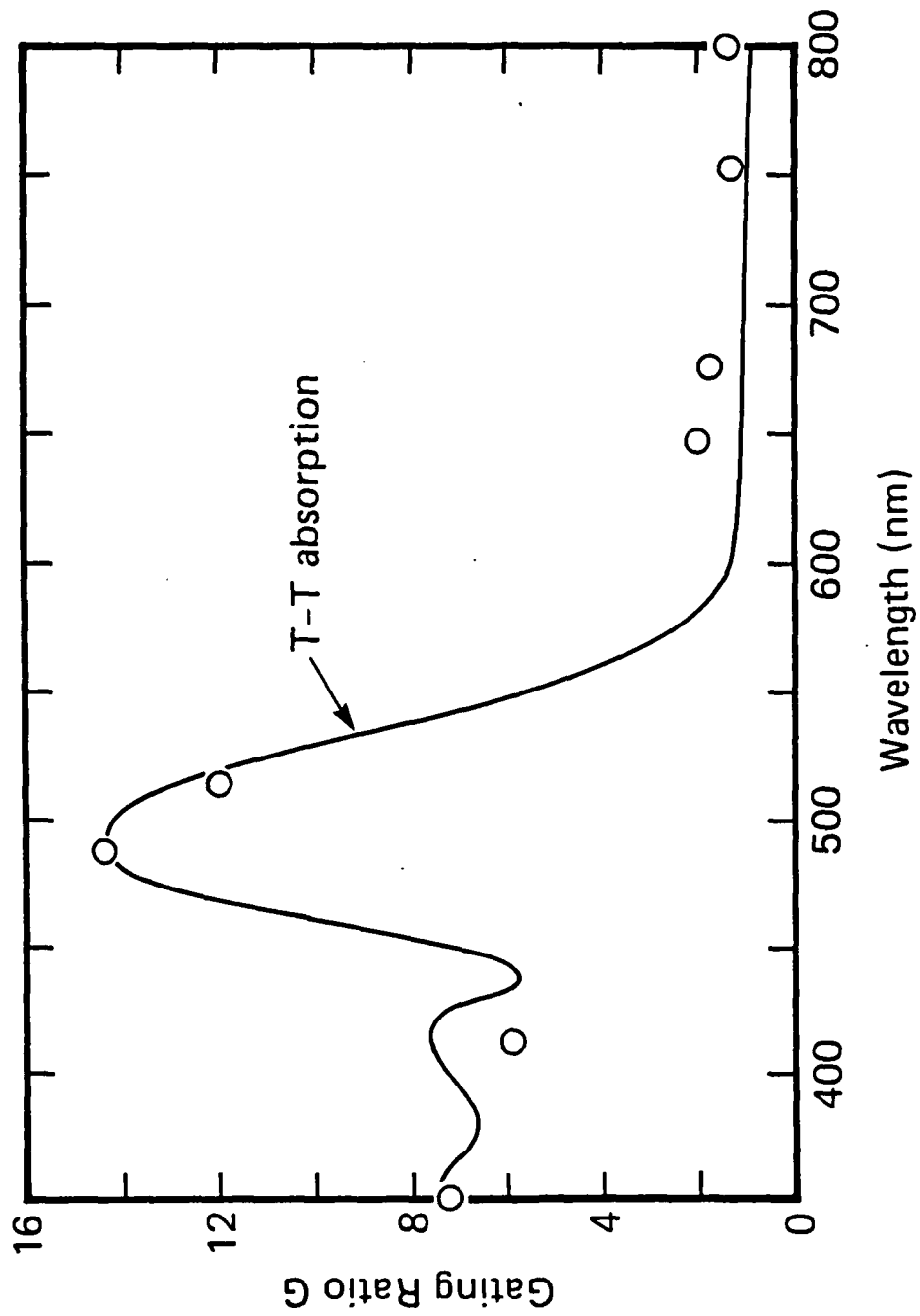
Figure 1

Figure 2

Figure 3

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